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Thermodynamics of hydrogen bonding and van der Waals interactions of organic solutes in solutions of imidazolium based ionic liquids: "Structure-property" relationships

Mikhail A. Varfolomeev*, Artashes A. Khachatrian, Bulat S. Akhmadeev, Boris N. Solomonov

Department of Physical Chemistry, Kazan Federal University, Kremlevskaya 18, Kazan 420008, Russia

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ABSTRACT

In the present work thermochemistry of intermolecular interactions of organic compounds in solutions of imidazolium based ionic liquids (ILs) has been studied using solution calorimetry method. Enthalpies of solution at infinite dilution of non-polar (alkanes, aromatic hydrocarbons) and polar (alcohols, amides, and etc.) organic solutes in two ionic liquids 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium trifluoromethanesulfonate were measured at 298.15 K. The scale of van der Waals interactions of imidazolium based ILs has been proposed on the basis of solution enthalpies of *n*-alkanes in their media. The effect of the cation and anion structure of ILs on the enthalpies of solvation was analyzed. Enthalpies of hydrogen bonding of organic solutes with imidazolium based ILs were determined. It has been shown that these values are close to zero for proton acceptor solutes. At the same time, enthalpies of hydrogen bonding of proton donor solutes with ionic liquids are increased depending the anion: tetrafluoroborate ≈ bis(trifluoromethylsulfonyl)imide < 2-(2-methoxyethoxy)ethyl sulfate < trifluoromethanesulfonate. Enthalpies of van der Waals interactions and hydrogen bonding in the solutions of imidazolium based ionic liquids were compared with the same data for molecular solvents.

1. Introduction

Development of new effective solvents for different industrial and technological applications is one of the important tasks of modern chemical science. These solvents should possess such properties like low volatility, low to no toxicity, non-flammable, as well as high thermal stability, all in accordance with both ecological and safety rules. Meanwhile, such solvents should have good solvation ability and selectivity for specific compounds or processes. Imidazolium-based ionic liquids (ImzILs) – a class of organic salts which are in a liquid state in a wide range of temperatures below the decomposition temperature – fulfill some of these requirements, being composed entirely of alkyl imidazolium cation and different anions. Depending upon the structure of both anions and cations, ImzILs can dissolve different substances including raw materials [1,2], wood [3,4], organic polymers [5], but to name a few. Their wide range in polarity allows them to be fully miscible with polar substances (water, amides, alcohols, etc.) [6–8], as well as able to dissolve non-polar compounds (aliphatic and aromatic hydrocarbons) [9]. This fact makes them useful in separation processes, for example, they showed good efficiency for separation of sulfur and nitrogen containing compounds from fuels [10–12]. Nowadays, it is possible to synthesize ImzILs tailored with specific properties in order to carry out dissolution of a certain compound or material by variation of anions and cations nature. However, general relationships between the solubility of different organic compounds and structure of ionic liquids should be known in order to undertake such procedure. Meanwhile, a substance's solubility in a given solvent is determined by the intermolecular interactions strength. Quantitative data on the intermolecular interactions strength of ionic liquids with organic compounds may prove useful for prediction of solubility and other physical-chemical properties related to their binary and ternary mixtures. Ionic liquids are capable of forming different types of intermolecular interactions, due to consisting of polar and nonpolar fragments. Regarding organic non-electrolyte solutes, van der Waals interactions and hydrogen bonding are the

* Corresponding author at: Chemical Institute, Kremlevskaya 18, 420008 Kazan, Russia.
E-mail addresses: vma.ksu@gmail.com, mikhail.varfolomeev@kpfu.ru (M.A. Varfolomeev).

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